

# PATENT SPECIFICATION

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NO DRAWINGS

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## COMPLETE SPECIFICATION

### Improvements in or relating to the Electrolytic Deposition of Metals

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5 State, United States of America, and both citizens of the United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to the electrolytic deposition of nickel and is particularly concerned with the production of bright, smooth and lustrous nickel deposits.

15 It has been known to modify acid nickel plating baths by the introduction therein of additives intended to produce bright nickel deposits. Among such additives there have been employed various types of substances in association with aromatic and aliphatic sulphonates, sulphonamides and sulphonimides. The aforesaid substances have included alkynes, alkenes, amines, alkyne amines, and 20 alkene amines. Such substances have in the molecule an allylic or vinyl group only, an acetylenic group only, or an active amino group only. It has also been proposed to employ compounds having in the same molecule an amino and an allyl or vinyl group.

25 While some of the known addition agents produce bright nickel deposits to some degree, they do not contribute to superior levelling coupled with ease of control. Furthermore, 30 because of the high concentration that was necessary for these compounds to produce the desired brightness and levelling, the ductility of the deposit was impaired. In some cases, as for example with the alkynols, the 35 deposit has a marked tendency to "skip plate", i.e. to prevent deposition of nickel at low current densities.

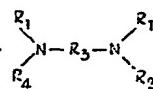
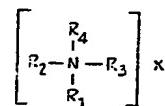
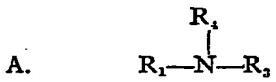
[Priority]

It is an object of the present invention to provide an aqueous acid nickel plating bath from which substantially level deposits may be obtained and which may reduce the low current density skip plate in the deposited nickel film.

45 According to the invention, there is provided an aqueous acid nickel electroplating bath having incorporated therein an amine having as substituents therein an alkene group and an alkyne group both attached to the same nitrogen atom.

50 It has been found that amines having these two groups attached to the same nitrogen atom impart superior levelling characteristics to the bath, with a substantial improvement in low current density characteristics of the nickel deposit. Relatively small amounts of these amines are effective and they do not substantially impair the ductility of the deposit.

55 These amines may have one of the following general structural formulae:



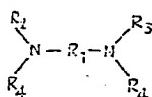
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## D.

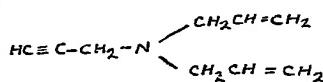
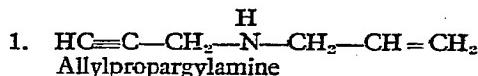
wherein  $R_1$  is an alkene group;  $R_3$  is an alkyne group;  $R_2$  and  $R_4$  are selected from hydrogen and alkene, alkyne, methyl, ethyl, propyl, phenyl and naphthyl groups; and  $X$  is an acid group, such as for example halogen, sulphonate or phosphate.

The compounds represented by general formulae C and D may be quaternized.

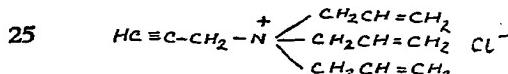
While each of the alkene and alkyne groups may contain up to 8 carbon atoms, alkene and alkyne groups containing up to 4 carbon atoms are considered to be more desirable. Together with the aforementioned

amines, other acetylenic compounds may be incorporated into the bath, so that a mixture of unsaturated compounds are employed.

The structural formulae given below are illustrative of the amines which may be employed in accordance with the invention:



Diallylpropargylamine



Triallylpropargylamine chloride

Examples of other amines which may be used are:

Vinylpropargylamine

30 Allyldipropargylamine

Divinylpropargylamine

Triallylpropargylamine chloride

bis[1:4-Allylamino]-2-butyne

bis[1:4-Diallylamino]-2-butyne

bis[1:4-Triallylamino]-2-butyne dichloride

The deposits resulting from baths contain-

ing the additives mentioned above have high lustre and are smooth with excellent levelling. In addition, the deposits do not exhibit low current density greyness which often occurs when additives such as amines or polyamines are used in the bath.

The amines employed in the present invention may be used singly or in mixtures or in the presence or absence of other types of additives. They may be used in standard Watts baths, all chloride baths, high chloride baths, all sulphate baths or sulphamate baths. Improved results may normally be obtained where there is incorporated therewith in the bath a sulphonlic acid, or a sulphonamide or sulphonimide. Examples of suitable sulphonlic acids, sulphonamides and sulphonimides are:

Benzene sulphonlic acid

Di-benzene sulphonlic acid

Vinylbenzene sulphonlic acid

Allylbenzene sulphonlic acid

Eromobenzene sulphonlic acid

1:5-Naphthalene disulphonlic acid

1:3:6-Naphthalene trisulphonlic acid

Saccharin sodium salt

Benzene sulphonamide

Dibenzene sulphonamide

Allyl sulfonamide.

The sulphonlic acids may be used in the form of a salt thereof with, for example, nickel, sodium or magnesium.

Typical standard nickel baths which may be employed in the invention are as follows in grams per litre:

Watts Bath	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	100—400
	$\text{NiCl}_2 \cdot 7\text{H}_2\text{O}$	5—80
	Wetting Agent	0—1
	Boric Acid	5—60
All Chloride Bath	$\text{NiCl}_2 \cdot 7\text{H}_2\text{O}$	50—200
	Boric Acid	0—50
	Wetting Agent	0—1

Among typical wetting agents which may be used are sodium lauryl sulphate, sodium 2-ethyl-hexyl sulphate and sodium octyl sulphonlic acid. The range of pH may be from 2.5 to 4.5 in usual practice.

The following Examples illustrate aqueous acid nickel electroplating baths, according to the invention from which bright, level and ductile deposits may be obtained. In the Examples the amounts are given in grams per litre of aqueous solution.

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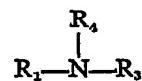
## EXAMPLE

Ingredient	1	2	3	4	5
Nickel sulphate	300	300	250	300	200
Nickel chloride	45	45	75	60	120
Boric acid	45	45	40	35	40
Saccharin			1.0		
Bromobenzene sulphonate		8			
1:5-Benzene disulphonate					15
Vinylbenzene sulphonate			0.6		
Sodium allyl sulphonate				0.5	
Sodium benzaldehyde sulphonate	2				
Dibenzene sulphonamide				1.5	
Allyl sulphonamide					1.5 0.5
3-Diallylaminopropyne-1				0.1	
Triallylpropargylamine chloride			0.04		
1-Allyl-3-amino-dipropyne	.06				
1-Allylamino-2-butyne					0.07
Allylpropargylamine			.03		
pH	4.2	4.3		3.6	4.0
Temp. °F.	135	140	140	135	155

- 5 The baths of the invention may be operated over a wide range of concentration, pH, and current densities. A pH of 3.0 to 4.8 is typical. The concentration of the additive may vary from 0.001 to 0.50 g. per litre when used in association with the sulpho-oxygen type materials such as sulphonic acids, sulphonamides and sulphonimides. The concentration of the sulpho-oxygen material will generally determine the concentration of the alkene-alkyne amine. When used alone, the concentration of the alkene-alkyne amine generally ranges from .001 to 1.0 g. per litre.
- 10 15 The baths may be operated with or without mechanical or air agitation. When air agitation is used, a compatible low-foaming or non-foaming type of wetting agent is preferably employed in the bath.
- 15 20 WHAT WE CLAIM IS:—
- An aqueous acid nickel electroplating

bath having incorporated therein an amine having as substituents therein an alkene group and an alkyne group both attached to the same nitrogen atom.

2. An aqueous acid nickel electroplating bath as claimed in Claim 1, wherein said amine has the general formula:



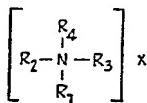
wherein  $R_1$  is an alkene group;  $R_3$  is an alkyne group; and  $R_4$  is selected from hydrogen and alkene, alkyne, methyl, ethyl and propyl groups.

3. An aqueous acid nickel electroplating bath as claimed in Claim 1, wherein said amine has the general formula:

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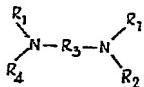
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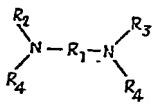
wherein  $R_1$  is an alkene group;  $R_2$  is an alkyne group and  $R_2$  and  $R_4$  are selected from hydrogen and alkene, alkyne, methyl, ethyl and propyl groups; and  $X$  is an acid group.

- 5 4. An aqueous acid nickel electroplating bath as claimed in Claim 1, wherein said amine has the general formula:



- 10 10. wherein  $R_1$  is an alkene group,  $R_2$  is an alkyne group; and  $R_2$  and  $R_4$  are selected from hydrogen and alkene, alkyne, methyl, ethyl and propyl groups.

- 15 15. An aqueous acid nickel electroplating bath as claimed in Claim 1, wherein said amine has the general formula:



wherein  $R_1$  is an alkene group;  $R_3$  is an alkyne group and  $R_2$  and  $R_4$  are selected from hydrogen and alkene, alkyne, methyl, ethyl and propyl groups. 20

6. A nickel electroplating bath as claimed in Claim 4 or 5, wherein said amine is quaternized. 25

7. An aqueous acid nickel electroplating bath as claimed in any preceding claim, wherein the alkene and alkyne groups contain up to 8 carbon atoms. 30

8. An aqueous acid nickel electroplating bath as claimed in any preceding claim, wherein the bath contains in addition a sulphonic acid, a sulphonamide or a sulphonimide. 35

9. An aqueous acid nickel electroplating bath, substantially as described with reference to any one of the foregoing Examples.

10. A method of electroplating a bright, level and ductile deposit of nickel, wherein there is employed an electroplating bath as claimed in any preceding claim. 40

11. A bright, level and ductile nickel deposit whenever produced by the method claimed in Claim 10.

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